

PATENT ABSTRACTS OF JAPAN

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(54) RESIN COMPOSITION, ADHESIVE COMPOSITION AND CURED PRODUCTS THEREOF

(57)Abstract:

PURPOSE: To obtain a resin composition comprising a vinyl ether compound, a polyester elastomer and a photo-cationic polymerization initiator, and providing photocurable adhesives excellent in adhesivity and water resistance and advantageous for the adhesion of plastics.

CONSTITUTION: A composition comprises (A) 20-90wt.% (especially 40-80wt.%) of a vinyl ether compound such as ethylene glycol divinyl ether, (B) 10-50wt.% (especially 15-35wt.%) of a linear polyester elastomer having a number-average mol.wt. of 5000-50000 (especially 10000-30000) and a glass transition point of $\leq 70^{\circ}\text{C}$, and (C) 0.1-10wt.% (especially 0.5-5wt.%) of a photo-cationic polymerization initiator such as bis{4-[di-(4-(2-hydroxyethyl)phenyl)sulfonyl]phenyl}sulfide bis-hexafluoroantimonate.

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CLAIMS

[Claim(s)]

[Claim 1] A resin constituent characterized by containing a vinyl ether compound (A), a polyester system elastomer (B), and an optical cationic initiator (C).

[Claim 2] An adhesives constituent characterized by containing a vinyl ether compound (A), a polyester system elastomer (B), and an optical cationic initiator (C).

[Claim 3] A hardened material of a constituent according to claim 1 or 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the resin constituent suitable for the adhesives on which it hardens by the exposure of light and adherend is pasted up.

[0002]

[Description of the Prior Art] There are many demands on which it is going to paste up a metal, plastics and plastics, plastics, a metal and glass, and plastics and glass by hardening by the exposure of light. When disliking that deformation by the heat of adherend produces it since hardening by the exposure of light does not need heating (for example, when a plastic-molding object serves as adherend), especially the request is strong. When adherend uses it for water as the bond strength of the physical properties required of such adhesives being natural, contacting, adhesives with which come out enough, and a certain thing is desirable, therefore the waterproof adhesive property, i.e., the holdout of the adhesive strength after being immersed in water, maintained balance in the adhesive property and the waterproof adhesive property in such a use are desired.

[0003]

[Problem(s) to be Solved by the Invention] This invention is excellent in the adhesive strength in an ordinary state, and the balance of a waterproof adhesive property, and aims at offer of the resin constituent suitable for the photo-curing mold adhesives which can be used in favor of adhesion of plastics.

[0004]

[Means for Solving the Problem] That is, this invention relates to a resin constituent characterized by containing a vinyl ether compound (A), a polyester system elastomer (B), and an optical cationic initiator (C), an adhesives constituent, and its hardened material. This invention is explained to details below. As an example of a vinyl ether compound (A) used by this invention For example, the ethylene glycol divinyl ether, the diethylene-glycol divinyl ether, The triethylene glycol divinyl ether, the tetraethylene glycol divinyl ether, The pentaethylene glycol divinyl ether, the dipropylene glycol divinyl ether, The cyclohexane dimethylol divinyl ether, the 1,4-butanediol divinyl ether, Cyclohexane dimethylol mono-vinyl ether, the trimethylol propane TORIBI nil ether, polyester polyvinyl ether, polyurethane polyvinyl ether, etc. can be mentioned. Among a resin constituent of this invention, 20 - 90 % of the weight is desirable especially desirable, and the amount of the (A) component used is 40 - 80 % of the weight.

[0005] In this invention, a linear-polyester-elastomer which can be guided, for example from a 2 base organic acid and dihydric alcohol can be mentioned as an example of a polyester system elastomer (B) to be used. As a 2 base organic acid, an adipic acid, isophthalic acid, a terephthalic acid, a phthalic acid, hydrogenation or a bromination phthalic acid, a sebacic acid, naphthalene dicarboxylic acid, etc. are mentioned, and a diethylene glycol, a propanediol, a butylene glycol, 1,6-hexanediol, 1,4-butanediol, neopentyl glycol, dipropylene glycol, a polypropylene glycol, a polyethylene glycol, a polytetramethylene glycol, an ethyleneoxide addition product of bisphenol A, etc. are mentioned as an example of representation as dihydric alcohol. 5,000-50,000 are desirable especially desirable, and number-average molecular weight of a polyester system elastomer (B) is 10,000-30,000. Moreover, an elastomer described here points out a material with flexibility and tenacity, and a thing 70 degrees C or less has a desirable glass transition point. A polyester

system elastomer is marketed and BAITERU (trade name) series (made in Goodyear), BAITERU PE-200 [for example,], and 207 grades are mentioned to the Toyobo Byron (trade name) series (Toyobo Co., Ltd. make) 103, 200, 300, 500, 560, 600, and 630, for example, Byron, and Byron GK 130, and a pan as the example. Among a resin constituent of this invention, 10 - 50 % of the weight is desirable especially desirable, and the amount of the (B) component used is 15 - 35 % of the weight.

[0006] As an example of an optical cationic initiator (C) used by this invention for example, screw [4-(G [4-(2-hydroxyethyl) phenyl] SURUHONIO) phenyl] sulfide screw-hexafluoro phosphate (the Asahi Denka Kogyo K.K. make --) SP-150, propylene carbonate 73% dilution article, and screw [4-(G [4-(2-hydroxyethyl) phenyl] SURUHONIO) phenyl] sulfide screw-hexafluoroantimonate (the Asahi Denka Kogyo K.K. make --) SP-170, propylene carbonate 40% dilution article, and screw [4-(diphenyl SURUHONIO) phenyl] sulfide screw-hexafluoro phosphate (the Degussa make --) Degacure KI85, 60 - 70% dilution article of propylene carbonate, triphenylsulfonium hexafluoroantimonate, aryl iodonium salt, an AREN ion complex (for example, IRUGAKYUA 261 (Ciba-Geigy make) etc. can be mentioned.) Among a constituent of this invention, 0.1 - 10 % of the weight is desirable especially desirable, and the amount of the (C) component used is 0.5 - 5 % of the weight.

[0007] It can dissolve and mix and a resin constituent of this invention can obtain each component of (A), (B), and the (C) component. A resin constituent of this invention in addition to said component 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 1,4-butanediol monochrome (meta) acrylate, Phenoxy ethyl (meta) acrylate, TORIBUROMO phenyl (meta) acrylate, TORIBUROMO phenoxy ethyl (meta) acrylate, o-phenylphenol poly (n=1-4) ethoxy (meta) acrylate, Acrylate (meta) of phenyl glycidyl ether, bisphenol A poly ethoxy (n=1-10) di(meth)acrylate, Bisphenol F poly ethoxy (n=1-10) di(meth)acrylate, Isobornyl (meta) acrylate, polyethylene GURIKORUJI (meta) acrylate, Ethylene GURIKORUJI (meta) acrylate, diethylene GURIKORUJI (meta) acrylate, 1, 6-hexane JIORUJI (meta) acrylate, nonane JIORUJI (meta) acrylate, Acrylate (meta) monomers, such as TORIMECHI roll pro pantry (meta) acrylate and ditrimethylol propane tetrapod (meta) acrylate, epoxy (meta) acrylate (for example, a reactant of a novolak mold epoxy resin and an acrylic acid (meta) --) A reactant of the bisphenol A mold epoxy resin and an acrylic acid (meta) etc., urethane (meta) acrylate (for example, ethylene glycol and neopentyl glycol --) A diethylene glycol, bisphenol A, poly ethoxy diol, A polypropylene glycol, a polybutylene glycol, a polytetramethylene glycol, Polyol and tolylene diisocyanate, such as polyester diol, polybutadiene polyol, and polycarbonate diol, The organic poly isocyanate and 2-hydroxyethyl (meta) acrylate, such as xylylene diisocyanate, isophorone diisocyanate, and hexamethylene diisocyanate, urethane (meta) acrylate which hydroxyl-group content (meta) acrylate, such as 2-hydroxypropyl (meta) acrylate and 1,4-butanediol monochrome (meta) acrylate, can be made to be able to react, and can be obtained -- etc. -- an acrylate (meta) compound and an epoxy resin (for example) a phenol novolak mold epoxy resin, a cresol novolak mold epoxy resin, the bisphenol A mold epoxy resin, a bisphenol female mold epoxy resin, cycloaliphatic epoxy resin, etc. -- etc. -- it can be used if needed.

[0008] When using the above and an acrylate (meta) compound, it is desirable to use an optical radical polymerization initiator (for example, 1-hydroxy cyclohexyl phenyl ketone, acetophenone dimethyl ketal, 2-hydroxy - 2-methyl-1-phenyl propane-1-ON, 2 and 4, 6-trimethyl benzoyl diphenyl phosphine oxide, etc.). As for these, it is desirable to use 0.1 - 10 weight section to the acrylate (meta) compound 100 weight section.

[0009] Moreover, a leveling agent, a defoaming agent, light stabilizer, an antioxidant, an ultraviolet ray absorbent, a flame retarder, polymerization inhibitor, an antistatic agent, a silane coupling agent, etc. can be used together.

[0010] A hardened material of a resin constituent of this invention can be obtained by irradiating ultraviolet rays at a resin constituent of this invention according to a conventional method. An adhesives constituent of this invention is very suitable to paste up iron, aluminum, a galvanized steel sheet, stainless steel, acrylic resin, ABS plastics, polyamide resin, polycarbonate resin, glass, etc. Of course, at least one side of adherend needs to be transparent to a degree to which exposure light may arrive at a covering side. In adhesion, an adhesives constituent of this invention is irradiated at adherend, about 10-500 micrometers irradiates light after spreading and in an adhesion side, and hardening adhesion is carried out. Ultraviolet rays emitted as a light which can be used from a high-pressure mercury lamp, a metal halide lamp, a low-pressure mercury lamp, etc. can be mentioned. A resin constituent of this invention can be used for a coating, a coating agent, a lens, etc. in addition to a use as adhesives.

[0011]

[Example] Next, an example explains this invention still more concretely.

Each component (a numeric value is the weight section) shown in one to example 5 table 1 was mixed with the paint roll using stirring equipment at a rate shown in a table 1, and the adhesives constituent was prepared. The performance test of these adhesives constituent was performed by pasting up an acrylic board and an aluminum plate.

[0012] The adhesion method: The ultraviolet rays of the energy of 1000 mJ/cm² were irradiated with the high-pressure mercury lamp, and hardening adhesion of each test piece was carried out.

Exfoliation adhesive-strength-test method: Adhesives are applied to an acrylic board with a width of 25mm, a length [of 150mm], and a thickness of 2mm, aluminum with a thickness of 100 micrometers is put on it so that the thickness of adhesives may be set to 80 micrometers, from the acrylic board side, the above-mentioned ultraviolet rays were irradiated and hardening adhesion of the adhesives was carried out. Thus, T form friction test was performed for the created test piece at the rate of speed-of-testing 50 mm/min.

O Exfoliation bond strength More than 500 g/cm^{**} Exfoliation bond strength 100-500g/cm^x Exfoliation bond strength 100 or less g/cm

[0013] Shearing adhesion-test method: Having used the weight portion of two acrylic boards with a width of 25mm, a length [of 150mm], and a thickness of 2mm as 25mmx25mm, adhesives were applied so that it might be set to 80 micrometers. After irradiating said ultraviolet rays and making this they carry out hardening adhesion, to it, shear bonding strength was measured by speed-of-testing 1 mm/min.

O Shearing bond strength 15kg/cm² Above ^{**} Shearing bond strength 5-15kg/cm^{2x} Shearing bond strength 5kg/cm² Following [0014] Water-resistant-test method: Water was filled to the vat made from stainless steel, and the test piece created by the above-mentioned method was immersed in it. This was left in 80-degree C oven for 24 hours, as water did not evaporate. Then, it took out from water and the friction test and the shear test were performed after 1-hour neglect.

[0015]

[A table 1]

Table 1 Fruit ^{**} Example 1 2 3 4 Five vinyl ether compounds (A)

Triethylene glycol divinyl ether 70 70 70 100 100 Cyclohexane dimethylol divinyl Ether 30 30 30 polyester elastomer (B)

Polyester (1) *1 20 30 50 Polyester (2) *2 20 Polyester (3) *3 20 light cationic initiator (C)

SP-170 *4 2 2 2 2, others beta - (3, 4-epoxycyclohexyl)

Ethyl trimethoxysilane 5 5 5 5 Exfoliation Bond Strength The first stage O O O O O After a water resistant test O O O O

^{**} shearing bond strength Early stages of O O O O O After a water resistant test O ^{**} ^{**} O^{**} [0016] *1 Polyester (1) :

the Toyobo Co., Ltd. make, Byron 550*2 Polyester (2): The Toyobo Co., Ltd. make, Byron 300*3 Polyester (3): The Toyobo Co., Ltd. make, Byron 1001-B*4 SP-170: The Asahi Denka Kogyo K.K. make, screw [4-(G [4-(2-hydroxyethyl) phenyl] SURUHONIO) phenyl] sulfide screw-hexafluoroantimonate (propylene carbonate 40% dilution article)

The hardened material of the resin constituent of this invention is excellent in bond strength and a water resisting property so that clearly from a table 1.

[0017]

[Effect of the Invention] The hardened material of the resin constituent of this invention is excellent in bond strength and a water resisting property, and fits especially adhesives.

[Translation done.]